MELTING POINTS OF THE REFRACTORY ELEMENTS— I. ELEMENTS OF ATOMIC WEIGHT FROM 48 TO 59

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The elements included in this list are the iron group—nickel, cobalt, iron, manganese, and chromium—and also vanadium and titanium. In subsequent papers results will be given on other refractory elements now being studied, and it is hoped eventually to include all the available refractory elements in this series of melting-point determinations.

The method mainly used is that of the micropyrometer [1] which, for those metals for which the melting is sharp, as nickel, cobalt, and iron, permits working to a precision of $1°$ or $2°$ with a few thousandths of a milligram of the material the melting point of which is sought.

An estimation of the melting points of the iron group elements [2] was made some years ago by a similar but less sensitive method at a time when none of these melting points was well known. The object of these earlier measurements was primarily to demonstrate the convenience and reliability of the method, especially for those elements which can be obtained pure only in minute quantities. It is believed that the present series of determinations, with the improved apparatus, will contribute to a more exact knowledge of these melting points.

The melts were taken for the most part in pure hydrogen generated from "hydrone," and further purified and dried by passing, in the order named, through a neutral lead nitrate aqueous solution with lead sulphate in suspension to remove sulphur and arsenic; through a solution of sodium hydroxide to remove carbon dioxide,

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[1] A Micropyrometer, by G. K. Burgess, Jl. Washington Academy, 3, p. 7; 1913. Phys. Zs., 14, p. 158; 1913. This Bulletin, 9, p. 575; 1913.

[2] Melting Points of the Iron Group Elements by a New Radiation Method, by G. K. Burgess. This Bulletin, 3, p. 345; 1907.

over fused calcium chloride for preliminary drying, over a platinum catalyzer, consisting of a spiral of 0.4 mm platinum wire 1 m long, heated electrically to incandescence to combine the oxygen in the hydrogen and remove arsenic and antimony.   It was finally dried by passing through a U tube containing calcium chloride, through concentrated sulphuric acid, and over phosphoric pentoxide.   Although this complete train may not be necessary for all the metals studied, yet in some cases, such as chromium and zirconium, pure, dry hydrogen appears essential to success.   For the more readily oxidizable metals, it was also found advisable, before admitting hydrogen, to first remove all air from the cold furnace with a vacuum pump.

The melts, except for titanium, were taken on platinum strips 6 to 8 cm long, 4 mm wide, and 0.01 or 0.02 mm thick.   Manganese was also melted on nickel strips and titanium was melted on iridium strips.   The melting points of nickel, cobalt, and iron were also taken in crucibles.

Calibration with Nickel and Palladium.—For melts on platinum the pyrometer was calibrated in terms of the melting points of nickel and palladium.   The melting of these metals is extremely sharp on platinum and they appear to show no alloying until they melt.   It is assumed that they melt on platinum at the same temperatures as in crucibles, which we have found to be the case within the limits of observational errors, for nickel, cobalt, and iron, the only metals thus compared.

Numerous observations were made with various metals upon the possible effects on the melting-point determinations of alloying with the platinum strip.   We are convinced that except possibly in some cases, which we shall not consider here, in which there may be a chemical reaction among the materials in the furnace, as, for example, when silicon, platinum, and hydrogen are together, there is no significant alloying effect with the apparatus and materials as we use them.   We may mention, for example, that with gold on a platinum strip it is possible to have two adjacent pieces of gold, differing in temperature by only 1°, one of which is completely liquid and the other showing no signs of melting.   (See Fig. 104.) Again, the alloying of silver with platinum may be examined and followed very readily under the microscope, since the silver appears

black before and also just after melting, and only begins to brighten, due to alloying, after melting has occurred, even with very minute particles of silver on the platinum strip.   Finally, Day and Sosman find that anorthite and palladium melt in crucibles at the same temperature.   We find this also true for the melting of these substances on platinum.   Moreover, we have exactly reproduced with the micropyrometer their value of the diopside melting point, 1391, with some of their material; thus proving that calibration with metals gives correct melting points of nonmetallic materials.

The melting points of both nickel and palladium may be considered as well established by several series of measurements, in particular by the gas thermometer measurements of Day and Sosman.[3]   The palladium point has also been determined several times by optical methods,[4] and the difference between nickel and palladium has been carefully measured.[5]

We have made an independent optical determination of the nickel melting point in hydrogen with an Arsem furnace.[6]   The nickel was melted in a magnesia crucible contained within an outglazed closed-end porcelain tube or one of kaolin.   Temperatures were measured with a Holborn-Kurlbaum form of Morse pyrometer which had been calibrated by Dr. Kanolt at the melting points of antimony (630), $Ag_3 - Cu_2$ (779), silver (960.5), copper (1083), and diopside (1391).   Five observations by Dr. Kanolt on the melting point of platinum with this pyrometer gave 1755 ± 5 in an iridium furnace, or in exact agreement with the generally accepted value.[7]

For nickel, four observations in hydrogen gave us 1449, 1450, 1449, 1449 in the Arsem furnace, by the method of optical heating and cooling curves,[8] which is close to Day and Sosman's value, 1452.   Four observations of the melting point of nickel on iridium with the micropyrometer gave us 1452.

With the long-filament pyrometer lamps used, the equation [9] $\log C = a + b \log T$ (in which $C = $ current, $T = $ absolute temperature,

[3] Day and Sosman, Carnegie Institution of Wash. Pub. No. 187; 1911.
[4] Waidner and Burgess, this Bulletin, 3; p. 163; 1907. Warburg and others, Berlin Akad , p. 35; 1913. Nernst and Wartenberg, Verh. Deutsch Phys. Ges., 8; p. 48; 1906.
[5] Ruer, Zs. Anorg Ch., 51; p. 223; 1906.
[6] J. Am. Chem. Soc., 28; p. 921; 1906.
[7] See Day and Sosman, loc. cit.; Waidner and Burgess, loc. cit.
[8] C. W. Kanolt, Techn. Paper No. 10, Bureau Standards; 1912.
[9] Pirani, Verh. Phys. Ges., 12; p. 323; 1910.

and *b* is very nearly unity) is sufficient for very considerable temperature ranges, and permits a calibration in terms of two temperatures only, i. e., nickel and palladium. Applying this equation by extrapolation to the determination of the platinum melting point by observing the melting of platinum strips mounted as usual for taking metal melts, we obtained 1755° ± 5 from six observations. The relatively small precision is due in part to the impossibility of perfectly controlling the rheostats and exactly matching lamp and strip at the instant the latter burns out and in part to the fact that the strip does not always melt at exactly the spot sighted upon.

We had originally intended to adopt a three-point calibration, and expected to use for this purpose nickel, cobalt, and palladium as determined by Day and Sosman, but we found it impossible to make the value of the cobalt point as determined by them fit the curve by some 10°, as will be shown later, and fortunately the two-parameter curve was found sufficiently exact.

The metals actually used for calibration in hydrogen were " Kahlbaum " electrolytic nickel (M. P. = 1452) and pure Heraeus palladium (M. P. = 1549), both of the same grade as used by Day and Sosman.[10] A sample of their palladium gave exactly the same melting point as ours. Palladium melts at the same temperature in air, vacuo, and hydrogen, according to our observations. In controlling the constancy of the pyrometer lamps and studying the reproductibility of the melts some 35 observations were taken of nickel and 20 of palladium. The various metals were not studied in regular order but mixed as indisciminately as possible, with observations on the standard points, nickel and palladium.

IRON

Pure electrolytic iron from three sources and as many different methods of preparation was used, namely, from Prof. C. F. Burgess (same iron used in the 1907 observations [11]) from Langheim-Pfanhauser Werke A. G. kindly furnished by Dr. Hans Goldscmidt, and

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[10] Day, Sosman, and Allen, loc. cit. The analysis by Dr. Allen of these products gave the nickel as 99.835 pure and the palladium 99.975.

[11] G. K. Burgess, loc. cit.

Mr. Wm. C. Cuntz, and from a sample prepared by Mr. J. R. Cain, of this Bureau. The analyses as furnished are as follows, not including gases:

	C. F. Burgess	Langheim-Pfanhauser	Cain
	Per cent	Per cent	Per cent
Sulphur..	0.00	0.00	0.004
Silicon..	.013	.00	.001
Phosphorus..	.004	.007	.0006
Manganese...	.00	.00	.0000
Carbon..	.012	.00	.004
Copper	....	.008	.008

"Kahlbaum" iron in powdered form and iron reduced on the platinum strip in hydrogen from "Kahlbaum" oxide were also used.

In Table 1 are given the results obtained in a hydrogen atmosphere with the micropyrometer.

TABLE 1

Melting Point of Iron by Micropyrometer

Electrolytic, C. F. Burgess	Electrolytic, Langheim-Pfanhauser	Electrolytic, Cain	Powder, "Kahlbaum"	From oxide, "Kahlbaum"
1538	1524	1533	1534	1532
1537	1532	....	....	....
1530	1534	....	....	....
1534	1534	....	....	....
1530	1535	....	....	....
1532	....	....	....	....
Mean, 1534	Mean, 1532	....	....	....

There appears to be no systematic difference among the several samples nor for different sized pieces, and the mean value is 1533 ± 1. This is somewhat higher than all other recent determinations. Carpenter, for instance,[12] assigns the value 1520 and in Landolt's tables (4th ed., 1912) the range is 1502 to 1532.

We venture to suggest that this apparently high determination of the iron point furnishes further evidence that the method here

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[12] H. C. H. Carpenter, Iron and Steel Inst.; September, 1908.

used does not give low results for metals alloying with platinum, even in those cases in which the addition of either metal to the other is known to lower the melting point as is the case for iron-platinum.

The melting and freezing points of iron, in vacuo and in hydrogen, were also taken in the Arsem furnace. Four observations in vacuo gave 1531, 1531, 1529, 1527, and two in hydrogen gave 1523, 1527.

COBALT

The cobalt used was cobalt "Kahlbaum" in the form of powder, Kahlbaum's würfeln, cobalt reduced in hydrogen on the platinum strip from "Kahlbaum" cobalt oxide, and a sample kindly furnished by Messrs. Day and Sosman, cut from material which had actually been used for their determinations and which was originally powdered cobalt "Kahlbaum" [13] shown by Dr. E. T. Allen to be 99.951 per cent cobalt.

The cobalt "Kahlbaum" and würfeln were observed simultaneously and no appreciable difference in their melting points was detected.

TABLE 2

Melting Point of Cobalt by Micropyrometer

"Kahlbaum" powder and würfeln together	Co from the oxide "Kahlbaum"	Day and Sosman's sample
1478	1475	1474
1479	1478	1478
1482		1478
1476		
1475		
1476		
1478		
Mean, 1478		

All these samples appear to have the same melting point, the mean value of which is 1477 ± 2. Three observations taken in the Arsem furnace, by the same method described for nickel, each gave for the melting point of cobalt 1478. Finally, two melts of cobalt on iridium gave with the micropyrometer 1477 and 1478.

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[13] Day, Sosman, and Allen, loc. cit.

The value of the cobalt point which Day and Sosman found is 1490 in a nitrogen atmosphere. They used powdered cobalt heated in crucibles of 22 cc in hydrogen, the nitrogen replacing hydrogen immediately preceding an observation. They consider their cobalt determinations less satisfactory than those of nickel. There is a possibility of oxidation of some of the powder which may be sufficient to raise the melting point (cf. chromium and vanadium). We hope later to be able to study the effects of the presence of oxides on the melting points of the iron-group elements.

CHROMIUM

Strictly pure chromium was not available, and it is difficult to locate exactly the melting points of an impure viscous substance. Observations were taken on two samples from Kahlbaum and on one from Dr. H. Goldschmidt, all of a purity probably not greater than 98 per cent.

TABLE 3

Melting Point of (98 Per Cent ?) Chromium by Micropyrometer

Kahlbaum I..................................	1527
Kahlbaum II.................................	1536, 1513, 1513
Goldschmidt.................................	1514, 1524

As best representative value we may take 1520, or a temperature slightly lower than the iron melting point, 1533. However, the melting point of pure chromium may well be above that of iron, as is shown by a consideration of the formula for lowering the freezing point by metallic impurities:

$$\Delta t = \frac{0.02 \cdot T^2 \cdot p}{\rho \cdot M}$$

when p = per cent impurity of molecular weight M, ρ = heat of fusion at absolute temperature T. Assuming that $\rho = 30$ and $M = 100$, we have $\Delta t = \dfrac{0.02 \cdot \overline{1800}^2 \cdot 2}{30 \cdot 100} = 43°$, so that assuming this formula to hold, which is questionable, the melting point of strictly pure chromium might be as high as 1560. On the other hand, the value 1520 may be nearer the true one if, as appears probable, the presence of oxides acts in the direction not of lowering

but of raising the chromium melting point, as was found in the case of vanadium by Ruff and Martin.[14] If chromium is melted, for example, in a slightly oxidizing atmosphere or in impure hydrogen, an apparent melting point above that of platinum may be obtained.

MANGANESE

We have not been able to obtain pure manganese, and the impure samples from Kahlbaum and from Goldschmidt are even more sluggish than chromium. The Goldschmidt manganese was from a sample furnished with the following analysis:

	Per cent.
Si	0. 70– 1. 00
Fe	.95– 1. 05
Al	.40– .70
S	.05– .10
P	.20– .30
Mn	97. 70–96. 90

Melts were taken both on platinum and on nickel strips with the micropyrometer using gold (1063) and palladium as calibration points. Those on nickel were less satisfactory, due apparently to evaporation of nickel.

TABLE 4

Melting Point of (97.5?) Manganese

Kahlbaum		Goldschmidt	
On Pt	1242	On Pt	1261
On Ni	1221	On Pt	1264
		On Pt	1279
		On Ni	1254

The mean is 1254, which is possibly lower than the melting point of strictly pure manganese by 20°.

VANADIUM

Dr. v. Wartenberg, of Berlin, was kind enough to send us some 97 per cent vanadium prepared by him from the suboxide by the alumino-thermic method with calcium. It contains traces of Ca, Al, and Fe. Prof. Wedekind, of Strassburg, also furnished us with a sample of his 98 per cent vanadium.

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[14] Ruff and Martin, Über reines Vanadin Zs Angew. Chem., **25,** p. 49; 1912.

We have also examined two samples purchased from Kahlbaum at different dates. None of the samples melt sharply, the substance being quite viscous, and they all show evidences of incipient melting many degrees below the temperature at which the melting is complete.

With the Kahlbaum samples, evidences of melting were apparent as low as 1500 and melting was complete at about 1720, the samples showing evidences of nonhomogeneity of composition.

With Dr. v. Wartenberg's and Prof. Wedekind's vanadium the following results were obtained:

TABLE 5

Melting Point of Vanadium by Micropyrometer

98 per cent Va from Wedekind	97 per cent Va from v. Wartenberg	
1700	1680	Pieces of about 0.001 mg
1757	1691	
1773	1691	
1717	1685	
	1699	Medium sized pieces
	1705	
	1725	Largest pieces

Evidences of incipient melting were apparent from about 1650 with both of these materials, and the vanadium of Prof. Wedekind appeared to be somewhat inhomogeneous.

Other determinations of the vanadium melting point are as follows:

Year	Author	Method	Va M. P.
1905	v. Bolton.............	Total photometric..	1680
1908	Vogel and Tammann..	Optical and thermoelectric Va containing 1.2 per cent Si....	1750
1910	v. Wartenberg	Optical in Tungsten furnace 97 per cent Va................	1710
1912	Ruff and Martin......	Optical, from oxides and carbide in solution...............	1715

According to the experiments of Ruff and Martin,[15] the presence of either an oxide or the carbide raises the vanadium melting point. As some oxide is usually present, its effect probably

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[15] Ruff and Martin, loc. cit.

neutralizes the lowering due to the slight amount of metallic impurities. We would place the vanadium melting point at about 1720, both from a consideration of our own and of other determinations.

TITANIUM

Prof. M. A. Hunter, of the Rensselaer Polytechnic Institute, was kind enough to place at our disposal a sample of pure titanium which he prepared from material furnished by the Titanium Alloy Manufacturing Co., of Niagara Falls. This titanium as analyzed by Prof. Hunter contains only a trace of iron and no other detectable impurity. Prof. Wedekind likewise kindly sent us two samples prepared by him and one by Dr. v. Wartenberg. The colloid titanium of Wedekind melted at 1503 to 1451, and his powdered titanium at 1452.

We also took observations on two samples from Kahlbaum, which were evidently from their behavior quite impure, showing evidences of considerable inhomogeneity and an extended melting range. For the Kahlbaum samples the following points were obtained: 1664, 1724, 1677, 1737, 1641.

The titanium of Hunter and of v. Wartenberg showed no signs of melting on platinum. The melting points of these samples were taken on iridium strips.

TABLE 6

Melting Point of Titanium by Mycropyrometer

Ti from Prof. Hunter	Ti from Dr. v. Wartenberg
1790	1778
1785	1807
1785	1815
Mean, 1787	**Mean, 1800**

These melting points are fairly sharp, and the location of the temperature was made by calibrating the micropyrometer for the iridium strip by taking observations on it of the melting of palladium (1549) and of platinum (1755).

SUMMARY .

We have shown that the micropyrometer may be made an instrument of precision for the determination of the melting points of refractory metals and salts; that in the case of the metals examined the effect of alloying of microscopic particles on platinum and iridium is inconsequential until after melting, which we have shown for nickel, cobalt, and iron to occur at the same temperature for minute particles on the strips as for considerable quantities in crucibles of magnesia.

Assuming the melting points of nickel to be 1452, palladium 1549, and platinum 1755, and the calibration curves of the pyrometer lamps of the form $\log C = a + b \log T$, for the range here studied, we have determined the melting points of Fe, Co, Cr, Mn, Va, and Ti with the micropyrometer and of Ni, Co, and Fe in quantity in the electric furnace, all melts having been taken in pure hydrogen and Fe also in vacuo. For Cr, Mn, and Va, strictly pure materials were not available, and we can but estimate the melting points of the pure elements.

TABLE 7

Melting Points of Elements of Atomic Weight 48 to 59

Metal	Melting point with micropyrometer	Purity	Probable melting point of pure element
Nickel	[16] 1452 [17] 1449	99.83₅	1452±3
Cobalt	1477±2 [18] 1478±1	99.95₁	1478±5
Iron	[19] 1533±1 [17] 1528	99.98±.01	1530±5
Manganese	1255	97–98	1260±20
Chromium	1520	98–99	1520 to > Fe?
Vanadium	1720	97–98	1720±30
Titanium	1794±12	99.9+	1795±15

[16] Assumed value on platinum strip; also observed value on iridium strip.
[17] Crucible melts in electric furnace.
[18] Crucible melts in electric furnace; also on iridium strip with micropyrometer.
[19] Five samples all agreeing to within 3°.

PHOTOMICROGRAPHS

The photomicrographs show the appearance of the material on the strips as it is taken out of the apparatus. The photographs of the cold strip were taken with a metallographic microscope using vertical illumination and a magnification of 25 diameters.

Photomicrograph No. 104 shows two pieces of gold separated by less than 1 mm, one melted the other not melted. The pieces were about the same size when put on the strip but the piece which had been melted appears larger because it flattens on melting. The difference in temperature between the pieces was probably less than 1° C and the temperature of the strip was held constant while several observations were recorded. We consider this to be an indication that alloying between the strip and a metal on the strip does not have any appreciable effect on the melting point of the metal.

The streaks appearing in micrograph No. 87, Kahlbaum titanium on a platinum strip, and No. 90, vanadium, are typical of impure substances. No such streaks have been observed with pure metals, but those elements which we know are pure gather into globules, as is shown in the micrographs of nickel, iron, and palladium.
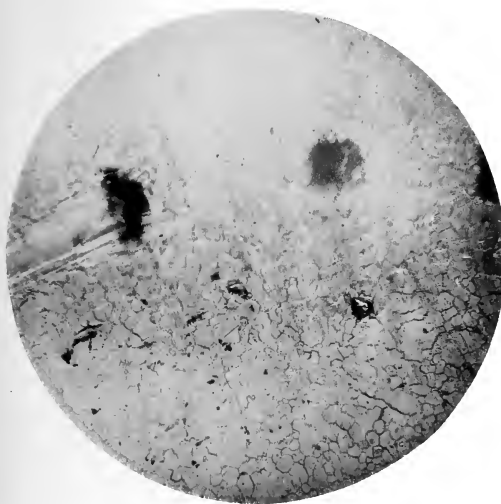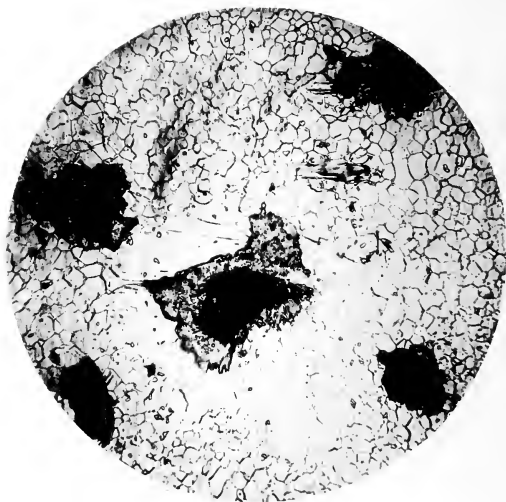
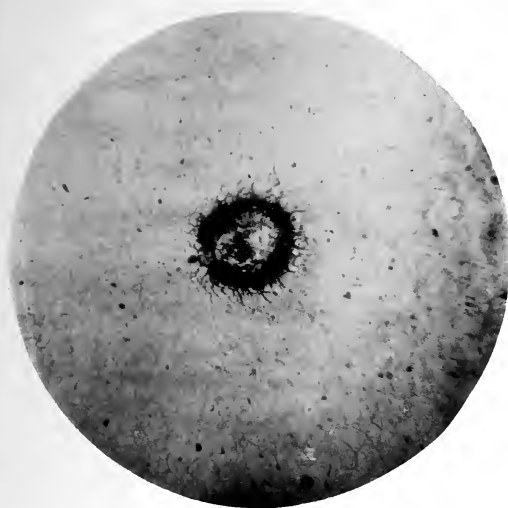WASHINGTON, April 25, 1913.
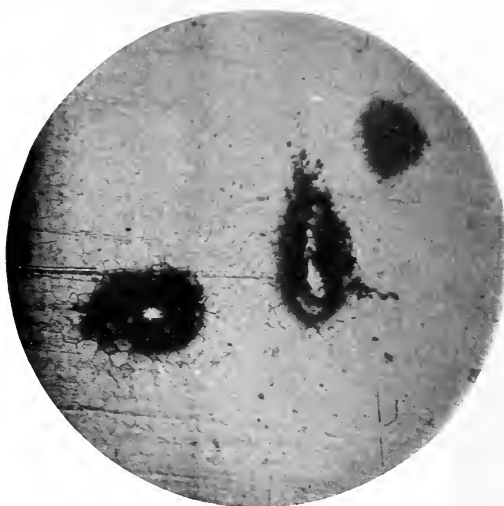
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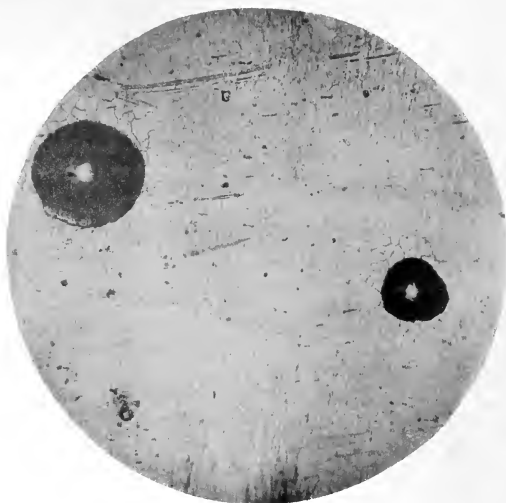
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NO. 87. TITANIUM. X 25.

NO. 90. VANADIUM. X 25.

NO. 207. CHROMIUM. X 25.

NO. 140. IRON. X 25.

PD.

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NO. 426. PALLADIUM PLATINUM TITANIUM } ON IR. X 25

NO. 437. PALLADIUM. X 25.